On the Exchange Properties of Allophanic Clays[1]

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THE ORIGIN OF THE EXCHANGE SITES on the clay minerals has been considered to be due to isomorphous replacement of Mg for Al in the octahedral layer and/or Al for Si in the tetrahedral layer and to the broken bonds at the edges of the crystals. The charges originated by the former mechanism are supposed to be pH-independent and are called permanent charges, while the charges due to the broken bonds are considered pH-dependent (Coleman and Mehlich, 1957). A more detailed classification of charges on the clay surface has been proposed by Mehlich (1960). These negative charges can be compared with acid groups of cation-exchange resins; the permanent charges resemble the strong acid groups, and the pH-dependent charges resemble the weak acid groups. The pH-dependent charges show stronger affinity for the hydrogen ions, so that only when the metal ion activity of the external solution becomes much greater than that of hydrogen ion activity can they be saturated with the metal ions. It is evident that the activity ratio of metal ions and hydrogen ions is the main factor that determines the degree of saturation with respect to the metal ions.

THEORETICAL

If an ion exchange reaction takes place according to the following equation:

$$HX + M^+ = MX + H^+ \quad \ldots\ldots \quad (1)$$

where X is the ion exchanger, an equilibrium equation is obtained:

$$K = \frac{(MX)\,(H^+)}{(HX)\,(M^+)} \quad \ldots\ldots\ldots \quad (2)$$

If (MX) and (HX) are expressed in terms of mole fractions of the cations occupying the exchange sites, it is reduced to Vanselow's exchange equation (1932), and K can be calculated from the measurable quantities.

If the exchange reaction is expressed as the sum of the following two reactions:

$$HX = H^+ + X^- \quad \ldots\ldots\ldots\ldots \quad (3)$$

and

$$X^- + M^+ = MX \quad \ldots\ldots\ldots\ldots \quad (4)$$

with Ka and Ks as their equilibrium constants:

$$Ka = (H^+)(X^-)/(HX) \quad \ldots\ldots \quad (5)$$

$$Ks = (M^+)(X^-)/(MX) \quad \ldots\ldots \quad (6)$$

then Equation (2) can be expressed as:

$$K = Ka/Ks = (MX)(H^+)/(HX)(M^+) \quad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

In equation (7), K is given as the ratio of two dissociation constants Ka and Ks. Assuming the exchange capacity is A, an expression of the degree of saturation of the exchanger with respect to M ions can be derived as follows:

$$(MX) + (MX) = A \quad \ldots\ldots\ldots \quad (8)$$

$$\frac{Ka}{Ks} = \frac{(MX)(H^+)}{[A - (MX)](M^+)} \quad \ldots \quad (9)$$

and, in rearranging the above equations, we have:

$$\frac{(MX)}{A} = \frac{1}{\dfrac{Ks(H^+)}{Ka(M^+)} + 1} \quad \ldots\ldots (10)$$

By arbitrarily setting values for Ks/Ka and $(H^+)/(M^+)$ of the equilibrium solution, a family of curves is obtained, as shown in Figure 1. If the exchanger contains two different acid functional groups with Ks/Ka of 10^4 and 10^8,

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respectively, in equal amounts, a curve with two inflection points (such as is shown in Fig. 1*A*) is obtained. This fact provides a possibility of characterizing different functional groups that may be present on the clay surface, if the constants Ks/Ka differ by a factor of 10^4 or greater.

It is important to note that in a given exchange material the factors governing the degree of saturation by a specific cation are the ratio of the cation and the relative affinity of the exchanger toward the cations, as expressed by the ratio Ks/Ka. If the acid functional groups are very weakly dissociable, it is impossible to saturate the exchanger by repeated treatment of the exchanger with the electrolyte solution unless the metal ion concentration of the solution is extremely high and the hydrogen ion concentration is extremely low.

EXPERIMENTAL PROCEDURE

A 1-g sample of soil or 0.2 g of soil colloid was placed in the carbon funnel and plugged with balls of filter pulp to serve as the filtering medium. A series of samples thus prepared were leached with 1N NaOAc solutions previously adjusted with NaOH or HOAc to give various pH values covering the range 4.5–10. Increments of the leachates were collected from time to time for pH measurements. Leaching was continued until the pH of the leachate became identical with or close to the value of the original solution. The samples were then leached with 150 ml of methyl alcohol while maintaining a 2–5 mm head over the sample. After the alcohol washing, the samples were leached with 1N NH_4OAc in the same manner, and the leachates were collected in 50 ml volumetric flasks. The sodium concentration was determined by flame photometry, using a Beckman DU spectrophotometer.

Poor buffering of the sodium acetate solution at higher pH range made it necessary to use unusually large amounts of leaching solution before the pH of the leachate approached that of the solution. Similar buffering problems were encountered in the acid range by Schofield (1949) and Iimura (1961) when ammonium chloride was used.

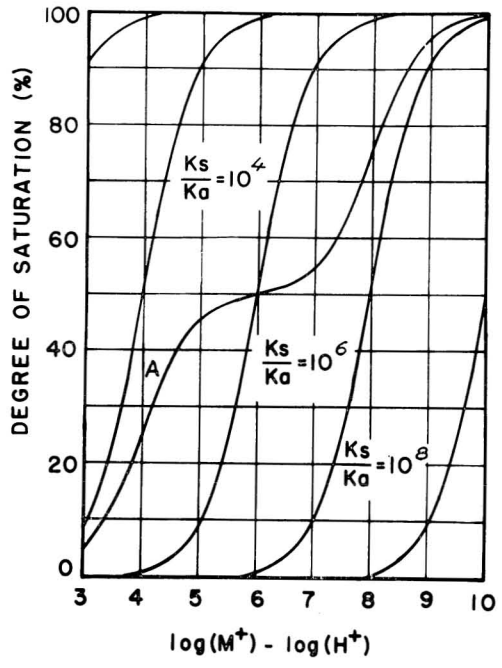

FIG. 1. Theoretical exchange curves. Curve *A* is the exchange curve of a hypothetical exchanger containing two kinds of acid functional groups in equal amounts, one with $Ks/Ka = 10^4$, the other with $Ks/Ka = 10^8$.

In the later part of this experiment, sodium carbonate solutions adjusted to the same pH value as that of the sodium acetate solutions were used prior to the leaching by sodium acetate solutions. Displacement of sodium carbonate solutions with sodium acetate solutions was necessary, since sodium carbonate is quite insoluble in alcohol.

MATERIALS

Silica gel. This sample, manufactured for chromatographic work, was obtained from the Baker Chemical Company. Particle size ranged from 0.18–0.07 mm. The appearance of a broad band near 3.7 Å on the X-ray diffraction pattern indicated that this material was essentially noncrystalline.

Halloysite. Sample mined in Eureka, Utah, and obtained through Ward's Natural Science Establishment, Inc.

Kaolin. Sample obtained through McKessen and Robbins, Inc.

Bentonite. Chiefly dioctahedral montmorillonite of uncertain origin, admixed with some quartz.

Soils. Samples of four soil profiles were collected from the slopes of Mauna Kea, island of Hawaii. All of these profiles have developed from volcanic ash, but their mineralogies vary considerably with changes in climate. One of the soils was of the Hanipoe series (Latosolic Brown Forest), two were of the Waimea series, hereafter referred to as Waikii and Mahoelua (Reddish Prairie), and the fourth was of the Waikaloa series (Reddish Brown). The soils have been listed in decreasing order of weathering. The first three soils were composed chiefly of noncrystalline colloids; halloysite was the main clay mineral in the Waikaloa series. These soils were treated with hydrogen peroxide to remove organic matter, washed with water, air-dried, and sieved through a 60-mesh screen. All soils used in this study have been described in the Soil Survey of the Territory of Hawaii, 1955.

Clay fractions. The $<1\mu$ fractions of these soils were separated, air-dried, and ground to pass a 100-mesh sieve.

Aluminum hydroxide A. Powder, obtained from Baker Chemical Company. X-ray diffraction pattern showed this to be pure gibbsite.

Aluminum hydroxide B. Precipitated from alkaline solution by carbon dioxide. Electrolytes were removed by prolonged dialysis and final removal was accomplished by electrodialysis. It was shown to be gibbsite.

Aluminum hydroxide C. Precipitated from alkaline solution by hydrochloric acid at a pH of about 7, washed with water and acetone, and air-dried. It was noncrystalline.

Aluminosilicate gels, A_1 and A_2. Mixed solutions of sodium silicate and sodium aluminate neutralized by carbon dioxide. The precipitate was washed free of electrolytes in Buchner funnels.

Aluminosilicate gels, B_1, B_2, B_3, and B_4. Mixed solutions of sodium silicate and sodium aluminate acidified to a pH of about 7 with hydrochloric acid. After standing overnight, they were washed in Buchner funnels until free of chloride ions. Acetone was used in the final washing.

RESULTS AND DISCUSSION

Clay Minerals and Allophanic Soils

The results obtained on clay minerals and allophanic soils are shown in Figures 2 and 4. All leaching solutions were 1N with respect to sodium ions, and it is fairly safe to take pH as the abscissa in lieu of log (M^+)–log (H^+). Without knowledge of the cation-exchange capacities, the amounts of sodium ions held on the exchanger were plotted against the pH of the final leachates.

As shown in Figure 2, the bentonite adsorbed the same amount of sodium ions regardless of the pH of leaching solutions. In comparing this curve with the theoretical curves shown in

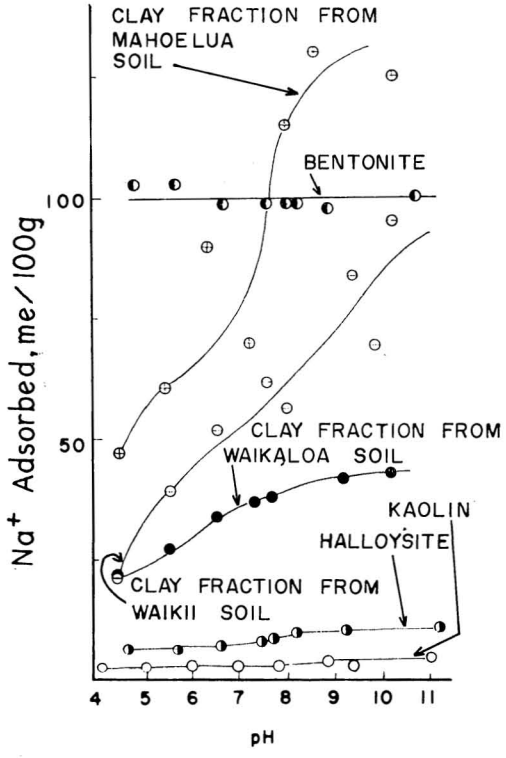

FIG. 2. Exchange curves of clay minerals and soil clays. ◐, Bentonite; ○, kaolin; ◑, halloysite; ⊖, clay fraction from Waikii soil; ⊕, clay fraction from Mahoelua soil, and ●, clay fraction from Waikaloa soil.

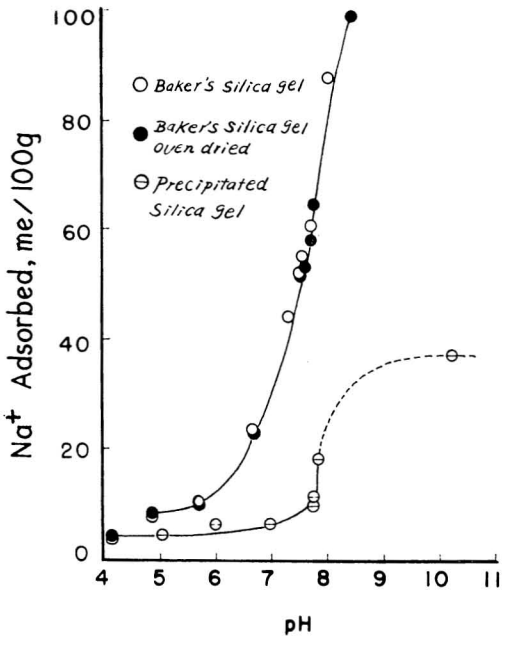

FIG. 3. Exchange curves of silica gels.

Figure 1, it is found that Ks/Ka for the acid functional groups of bentonite is about 10^2 or less. This implies that sodium ions are held on the montmorillonite clay with the same affinity as are the hydrogen ions. The amount of sodium ions adsorbed by halloysite and kaolinite is very small and partly pH-dependent. The inflection points near pH 8 indicate that the acid-functional groups of the pH-dependent part have a Ks/Ka value of about 10^8. The hydrogen ions associated with these functional groups cannot be replaced by sodium ions unless the $(Na^+)/(H^+)$ ratio of the solution becomes greater than 10^{10}. This suggests covalent bond formation between the functional groups and the hydrogen ions; simple ionic interraction between the negative charges and the hydrogen ions seems to be inadequate to explain this phenomenon. A comparison of these curves with those of silica gels shown in Figure 3 indicates that these charges on kaolinite and halloysite most probably are due to the surface hydroxyls attached to silicon atoms.

Aluminum Hydroxides

Aluminum hydroxides A and B both failed to show cation exchange to an extent that could be considered of real importance. The amount of sodium ions adsorbed under the pH range studied were always less than 1 me. per 100 g. Aluminum hydroxide C had a maximum exchange capacity of about 6 me. per 100 g, showing an inflection point near pH 8. The amount of sodium ions adsorbed at pH 4.5 was about 1 me. per 100 g.

Synthetic Aluminosilicate Gels

That the tetrahedrally coordinated aluminum atoms produce exchange sites was suggested by Iler (1955), and by De Kimpe, Gastuche and Brindley (1961). Such tetrahedrally coordinated aluminum atoms were postulated as the source of exchange capacity of soil allophanes by Iimura (1961). In this investigation, the aluminosilicate gels studied were prepared from alkaline solutions so as to arrange the aluminum atoms in the tetrahedrally coordinated positions, as much as possible. Their compositions, as well as the maximum cation exchange capacities, are listed in Table 1. Their exchange curves are shown in Figure 5.

It is striking that the CEC/Al ratios of the gels with silica-alumina ratios greater than 0.7 are very close to 1, indicating that each negative charge on the gel is associated with one aluminum atom. If the CEC of the gel is entirely attributed to the tetrahedrally coordinated aluminum atoms in gel A_2, it turns out that about 60% of the tetrahedral positions in the gel are occupied by the aluminum atoms. In gel A_1 the same calculation reveals that the tetrahedral positions occupied by the aluminum atoms would be as high as 62%, and that this amount may be the practical limit for the aluminum atoms to take the tetrahedral positions in the aluminosilicate gels under the specified conditions of preparation. Iler (1955), on the other hand, states that the maximum amount of aluminum atoms which can be tetrahedrally coordinated in the aluminosilicate gels is 50%.

The surface silanol groups of these synthetic gels apparently do not dissociate under the conditions of the experiment, and thus do not contribute to the CEC. The negative charges caused by these tetrahedrally coordinated aluminum atoms are relatively strong in acid character (that is, readily dissociable), and their

presence seems to suppress the dissociation of the surface silanol groups.

Comparison of Sodium Adsorption with Ammonium Adsorption

The same procedure was applied to the Hanipoe surface soil, using 1N NH_4Cl and 1N NH_4OAc solutions. Concentrated ammonia and hydrochloric acid solutions were used to adjust the pH values of NH_4Cl solutions; concentrated ammonia solution and glacial acetic acid were used to adjust the pH values of NH_4OAc solutions. The final total concentration of NH_4^+ ions was not 1N, but varied according to the desired pH values of the solutions. The results are shown in Figure 6.

The soil adsorbed about the same amount of sodium and ammonium ions up to pH 7 with acetate solutions. The amount of sodium ions adsorbed beyond pH 7 increased rapidly with increase in pH, while the amount of ammonium ions adsorbed tended to level off beyond this point. Adsorption from NH_4Cl and NH_4OAc solution followed similar patterns, but adsorption from the latter was significantly greater. The influence of anions on the amount of cation adsorbed by clays is well known, but as yet there seems to be no adequate explanation. Iimura (1961) showed that the amount of ammonium ions adsorbed increased with pH, following the same pattern of sodium adsorption by allophanic clays obtained in this study. The discrepancy seems to be due to the difference in the experimental procedures employed. His procedure was essentially that of Schofield (1949), under whose method the amount of ammonium ions adsorbed was determined without the removal of the excess salt present, while in the procedure used in this study excess salt was removed by alcohol and the ammonium ions adsorbed were apparently removed as the excess salt was removed from the system. This may be explained as follows:

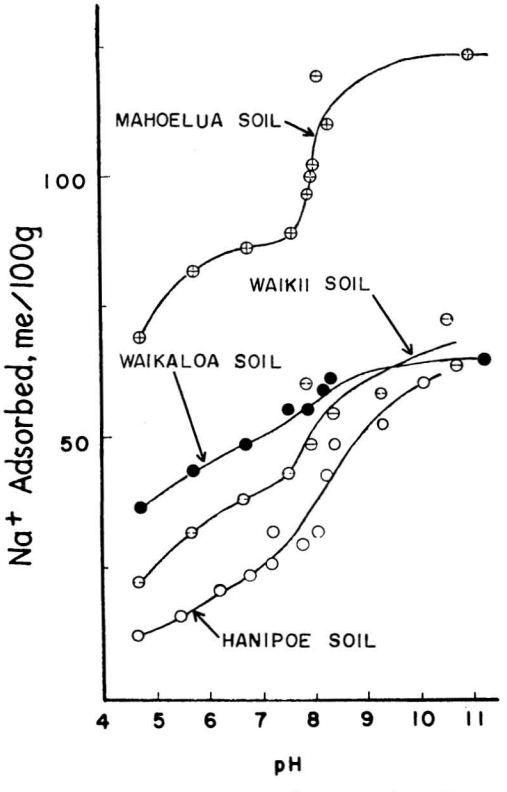

FIG. 4. Exchange curves of allophanic soils. ○, Hanipoe soil; ⊖, Waikii soil; ⊕, Mahoelua soil; and ●, Waikaloa soil.

Since the hydronium ion activity is very low in a solution having a pH of 8 and above, the following equilibrium tends to shift to the right:

$$NH_4^+ + H_2O = NH_3 + H_3O^+ \quad (11)$$

When protons of the silanol groups are replaced by ammonium ions, the ammonium ions will be strongly polarized so that they will split more or less distinctly into ammonia molecules and protons, the protons being strongly attracted toward the oxygen atoms on silicon atoms. Considering the equilibria

$$NH_3 + H_2O = NH_4^+ + OH^- \quad (12)$$

and

$$2H_2O = H_3O^+ + OH^- \quad (13)$$

with equilibrium constants of 1.8×10^{-5} and 10^{-14}, respectively, the equilibrium constant for (11) will be $10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$. The equilibrium constant for the equilibrium

$$NH_4^+ + H_2O + (-Si)-OH =$$
$$(-Si)-OH.NH_3 - H_3O^+ \quad (14)$$

is less than 10^{-8}, as can be seen by comparing the results in Figure 6 with those in Figure 1. It may be concluded that the ammonium ions

TABLE 1

COMPOSITION AND CEC OF SYNTHETIC GELS (AIR-DRIED BASIS)*

	A_1	A_2	B_1	B_2	B_3	B_4
SiO_2	8.99	30.82	32.51	41.58	46.53	48.38
Al_2O_3	24.92	22.96	20.72	12.54	9.46	7.48
H_2O (LOI)	11.86	7.64	6.69	6.88	5.86	5.07
H_2O—	47.03	25.89	27.64	29.21	30.87	34.18
Total	92.80	87.31	87.56	20.21	92.54	95.11
Na_2O (by difference)	7.20	12.69	12.44	9.79	7.46	4.89
Si/Al	0.306	0.671	1.382	2.814	4.159	5.487
CEC(me./100 g)	245	455	420	292	190	120
CEC/Al	0.501	1.01	1.03	1.19	1.02	0.82
Approx. inflection point, pH	6	5	5	6 and 4	4	4

* Analyst, Mr. H. Tenma.

held on the silanol groups are in fact partly ammonium ions and partly ammonia molecules. The equilibrium in (14) is strongly favored to the left, and, as excess ammonium ions are removed from the equilibrium system, ammonia is liberated into the washing alcohol, dissolving in it as ammonia molecules. This is quite different from the loss due to hydrolysis, in which cations are lost by replacement with protons produced by the dissociation of the dispersing medium, usually water. Dissociation of sodium ions into the washing alcohol seems to be prevented, probably because the proton activity in alcohol is too small to cause hydrolysis.

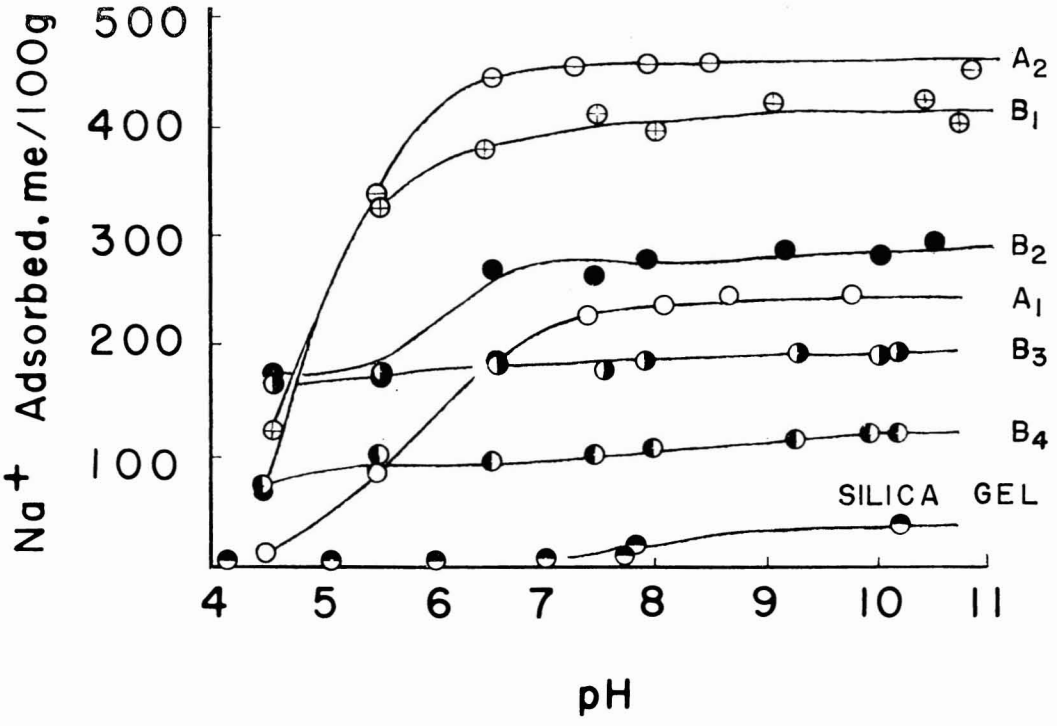

FIG. 5. Exchange curves of synthetic aluminosilicate gels and a silica gel. From top, A_2 (⊖), B_1 (⊕), B_2 (●), A_1 (○), B_3 (◑), B_4 (◐) and silica gel (◓).

It may be considered that the pH-dependent charges produce strong polarizing effect on hydronium ions, so that the protons are detached from the water molecules and bonded to the oxygen atoms of the aluminosilicate exchanger, forming hydroxyl groups. Permanent charges are not polarizing, so that hydronium ions neutralizing them remain as such in the system. Therefore, the hydronium ions on the permanent charge sites can be readily replaced by other cations, but the protons on the silanol groups are not so easily replaced. In this connection, it may be considered that the charges arising on the surface of the exchanger will have a stronger polarizing effect on the hydronium ions, while the charges arising inside the exchanger will have a weaker polarizing effect. The charges due to the broken bonds and surface hydroxyls will be pH-dependent, and the charges due to isomorphous replacement can be pH-dependent or permanent, depending on the distance from the surface of the exchanger to the site where the isomorphous replacement takes place. Here, permanent charges can be defined as the charges which do not give strong polarizing effect on neutralizing ions, and the pH-dependent charges are those which give strong polarizing effect on the neutralizing ions.

It may be concluded that the charges of the allophanic clays of the soils studied are due mostly to the surface silanol groups and tetrahedrally-coordinated aluminum atoms. The former charges show weak acidic character, the latter strong acid character. Contribution of the hydroxyl groups of aluminum hydroxide to the total exchange capacity seems to be insignificant.

It is quite unlikely that the silanol groups of the soil colloids will contribute to cation exchange of a soil under natural conditions, except in saline and alkaline soils. It is considered more desirable for most practical purposes to express cation exchange determinations in terms of permanent charges.

SUMMARY

1. Cation exchange in soils is considered to be an equilibrium reaction between the clay acid and the clay salt, assuming that the hydrogen-saturated and metal ion-saturated clays behave as if they were weak acid and salt, respectively.

2. Comparisons of the exchange curves obtained on clay minerals, allophanic clays, soils, and on synthetic silica, aluminosilicate, and aluminum hydroxide gels indicated that the so-called pH-dependent charges of the clays were most likely due to the dissociation of surface hydroxyl groups associated with silicon atoms (silanol groups), and that the so-called permanent charges were due to isomorphous replacement. In synthetic gels and the allophanic clays, the permanent charges were most probably due to tetrahedrally coordinated aluminum atoms in the aluminosilica network.

3. The lower exchange capacity obtained with NH_4^+ ions at higher pH values is explained on the basis that competition of protons between the pH-dependent charges and the ammonia molecules resulted in dissociation of NH_4^+ ions to protons and ammonia molecules,

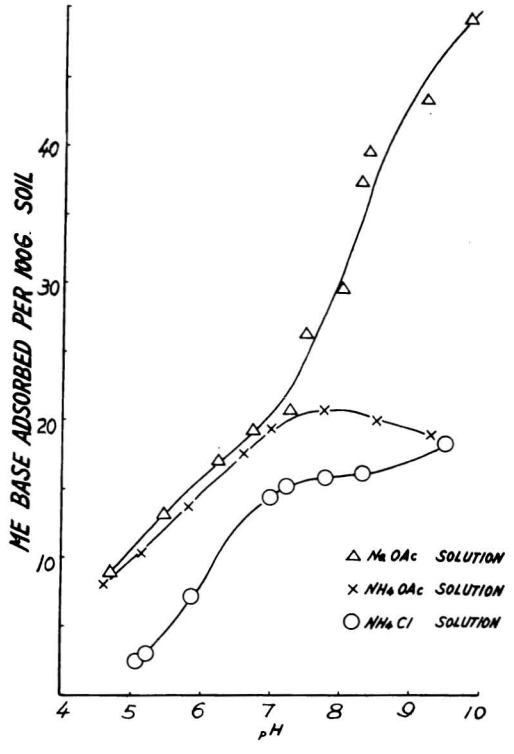

FIG. 6. Exchange curves of Hanipoe soil using different saturation solutions.

which resulted in the loss of ammonia upon removal of the excess salt.

4. It is suggested that the amount of exchangeable bases should be expressed in terms of percentage of the permanent charges, since the pH-dependent charges were considered not to take part in the exchange reaction under normal soil conditions.

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